Origin of nanosized diamonds in interstellar space and low-pressure-temperature Earth rocks

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Nanosized diamond particles in the interstellar space and in the Earth rocks related with water presence. In the paper proposed the model of the nanosized diamond particle formation oxidized water-carbon dioxide gaseous mixtures.

The origin of diamonds in interstellar space has been a topic of intense discussion since the discovery of presolar nanodiamonds in chondrites[1]. Meteoritic nanodiamonds provide information on the nucleosynthesis of evolved stars and the evolution of the astrophysical environment from which the solar system formed. Sellgren[2] identified the relationship between the interstellar diamond and water ice. Nakano et al.[3] related interstellar diamond formation with organic matter. Follow from these relationships Kouch et al.[4] identified new formation routes of diamond in interstellar clouds and parent bodies of carbonaceous chondrites in laboratory experiments. It's the ice mixture of H2O, CO, NH3, and CH4 (4 : 2 : 2 : 1).

The formation of the bulk of Earth diamonds is due to the deep upper mantle rocks - kimberlites formed at P and T corresponded to diamond thermodynamic stability. Meanwhile in the last 40 years micro- and nanodiamonds have also been founded in shallow earth rocks formed at P-T parameters corresponded to graphite thermodynamic stability[5-9] including the organic matrix[10-11]. The maximum diamond grade is observed in hydrothermal metasomatic zones of Kokchetave metamorphic massive situated in Northern Kazakhstan[12]. These diamonds have anomaly high concentration of N in comparing with kimberlitic, their main mineral inclusions are graphite, carbonate and water[13].

For diamond, it has been argued that crystallization in a P-T regime where diamond is actually thermodynamically unstable with respect to graphite, may be possible due to kinetic factors[14,15]. Nanosize diamond particles have energetic preference upon graphitic particles of the same size and could be more stable at low P-T parameters[16-19].

Fedoseev et al.[20] show that critical radii of graphite and diamond nuclei depends upon to surface energy (σ), atomic volume of carbon (V) and chemical potential of the resaturation ($\Delta\mu$):

$$r_g/r_d = V_g\sigma_g\,\Delta\mu_d / V_d\sigma_d\,\Delta\mu_g \qquad (1)$$

σ of nanosized diamond (d) and graphite (g) particles depends upon temperature and size of the particles[21]. From the σ_g/σ_d relation given in[22] and from (ref.18) it follows that for nanoparticles $V_g\sigma_g/V_d\sigma_d \approx 1$. Than r_g/r_d ratio could be expressed as:

$$r_g/r_d = \Delta\mu_d / \Delta\mu_g \qquad (2)$$

From another side chemical potentials of the resaturation for diamond and graphite could be expressed by the next formulations:

$$\Delta\mu_g = RT\ln(Pi/Pi_g) \qquad (3)$$

$$\Delta\mu_d = RT\ln(Pi/Pi_d) \qquad (4)$$

where Pi and $Pi_{g,d}$ are the real and equilibrium pressures of carbonaceous gases

As it follows from equations (2-4), (r_g / r_d) is connected with the ratio between real and calculated equilibrium pressures of carbonaceous gases. In the field of graphite stability $Pi_g < Pi_d$, which corresponds to preferable graphite formation from fluid phase. The condition of preferable diamond formation corresponds to $Pi_g > Pi_d$. The difference between $\Delta\mu_g$ and $\Delta\mu_d$ depends upon the difference of Pi/Pi_g and Pi/Pi_d and

at lower Pi_{car} it tends to zero, which corresponds to optimal condition of diamond formation from gaseous in the field of graphite stability.

In the hydrocarbon-hydrogen mixture the gas-solid reaction of hydrocarbon distruction could be proposed for carbon formation in a fluid:

$$CH_4 \rightarrow C + 2H_2 \qquad (I)$$

At high temperatures equilibrated pressure of hydrogen would be greater than equilibrated pressure of methane and in vacuum $P_{CH4(d)}$ tends to $P_{CH4(g)}$. The predomination of hydrogen under hydrocarbon in the gaseous mixture is also suppressed the growth rate of graphite more than it suppressed the growth rate of diamond (ref.15). As a result, it could stabilize the diamond growth at these conditions. Follow from this effect, Deryagin and Fedoseev (ref.14) have provided the diamond growth on the diamond seeds at vacuum conditions.

Subsequent work has shown that the addition of oxygen to the hydrocarbon gases can stabilize the diamond nucleus formation in the P-T field of graphite stability[23]. Bachman et al.[24] have shown that the synthesis of diamonds under metastable conditions corresponds to the narrow fluid composition in the C-O-H system. Calculations done for this system show that $P_{CH4(car)}$ is very low in the water and carbon dioxide stability fields of the system, closed to upper limit of carbon stability by oxygen (CCO buffer)[25]. In these fields at lower pressure and temperature $P_{CH4(g)} \approx P_{CH4(d)}$ which corresponds to diamond nucleus stabilization -Fig.1. This conclusion coincides with the established fact that diamond is more stable in an oxygen environment than graphite because oxygen reduces graphite to a greater degree than diamond[26]. From this scheme, we can explain the relationship of interstellar and Kokchetave diamonds with water.

Noteworthy for metastable diamond formation is the role of nitrogen[27,28]. It presents in interstellar clouds and parent bodies of carbonaceous chondrites associated with nanodiamonds (ref. 3,4) and in extra-high concentration in Kokchetave diamonds[29,30]. From another side, it's known that N is the main crystallochemical mixture in diamonds[31] and it has stabilization role at the diamond synthesis at high P-T conditions. The experiments provided at 500°C and total pressure of nearly 1000 bar show that nitrogen presence stabilized the diamond formation at these conditions[32,33]. It explains the high concentration of N in Kokchetave diamonds and correlation of ammonium with meteorite and interstellar nanodiamonds.

As a result, it is possible to conclude that nanosized diamond particles could be formed from carbon-bearing fluids at low temperatures and pressures without seeds. The nano- and microdiamonds detected in shallow deep Earth rocks, meteorites and interstellar clouds could be formed from fluids at low P-T parameters corresponding to graphite stability.

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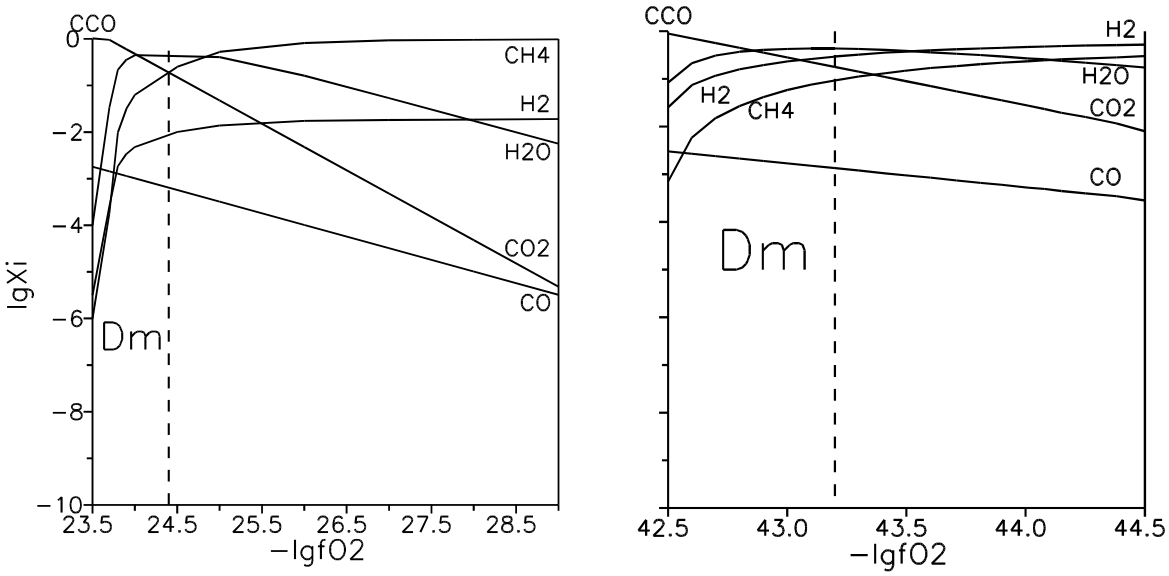
FIGURE CAPTIONS:

Fig. 1. Variation of compositions of C-O-H system : A. - at 500^{o} C and 10^{3} atm , B - at 250^{o} C and 10^{-3} atm. CCO- upper limit of carbon by oxygen, Dm – field of diamond preferable growth, point line – the boundary of this field.



A B

Fig..1